NASA TECHNICAL TRANSLATION NASA TT F-15,995

EFFECT OF COMPOSITION ON STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN SEVERAL CONCENTRATIONS OF BOILING $MgCl_2$ SOLUTIONS

M. Kowaka and T. Kudō

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(NASA-TT-F-15995) EFFECT OF COMPOSITION ON STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN SEVERAL CONCENTRATIONS OF BOILING (Kanner (Leo) Associates) CSCL 11F G3/26

N75-10207

Unclas 52671

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 NOVEMBER 1974

STANDARD TITLE PAGE

1. Report No. NASA TT F-15,995	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle EFFECT OF COMPOSITION ON STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN SEVERAL CONCENTRATIONS OF BOILING $MgCl_2$ SOLUTIONS		5. Report Date November, 1974
		6. Performing Organization Code
7. Author(s) M. Kowaka, and T. Kudō, Central Research Laboratories, Sumitomo Metal Industries, Ltd., Amagasaki, Japan		8. Performing Organization Report No.
		10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASw-2481
		13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Shujo nōdo no futtō $MgCl_2$ yōekichū ni okeru ōsūtenaito kei sutenresu kō no ōryoku fushoku ware ni oyobosu seibun genso no eikyō," Japan Institute of Metals, Journal, Vol. 37, Dec. 1973, pp. 1320-1329

16. Abstract The effect of composition on stress corrosion cracking of austenitic stainless steels has been investigated for several concentrations of boiling $MgCl_2$ solutions. The stress was applied by a constant load of 25 kg/mm^2. The relation between the boiling point of $MgCl_2$ solutions (concentration of $MgCl_2$ solutions) and the fracture time was determined. The results obtained are as follows: (1) The boiling point of $MgCl_2$ solutions at which the sensitivity to stress corrosion cracking is maximum decreases with increasing amounts of carbon and silicon in stainless steels. (2) With increasing amounts of molybdenum, nitrogen, phosphorus, chromium and copper, the boiling point increases. (3) Increase in nickel concentration decreases sensitivity to stress corrosion cracking in the overall concentration range of boiling $MgCl_2$ solution. Both the periods of induction and propagation were determined by measuring potential change of 304 and 316 stainless steels in boiling $MgCl_2$ solutions.

17. Key Words (Selected by Author(s)) PRICES SUBJECT TO CHANGE	18. Distribution Statement Unclassified-Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages	22. Price

NASA-HQ

EFFECT OF COMPOSITION ON STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN SEVERAL CONCENTRATIONS OF BOILING $MgCl_2$ SOLUTIONS

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I. Introduction /1320*

Numerous research results have been reported in the past concerning stress corrosion cracking of austenitic stainless steels in high concentrations of chloride solutions. Most of these have used boiling 42% $MgCl_2$ solutions[1] (154°C) as the accelerating test liquid, and there are few studies which have studied the cracking susceptibility of materials with attention focused on the environmental factors. Nevertheless, in view of the fact that stress corrosion cracking is a phenomenon which occurs when there are interrelations between the material factors, the stress factors, and the environmental factors, especially between the material factors and the environmental factors, it would be extremely problematical to make an evaluation of the cracking susceptibility of a material without taking the environmental factors into consideration. For example, it has been clearly established that in a boiling 42% $MgCl_2$ solution, Ni, C, and Si reduce remarkably the cracking susceptibility [1-7]. However, in certain actual environments, the cracking susceptibility is not necessarily reduced even when the Si contents are increased. This fact indicates that the environmental factors cannot be ignored in evaluating the cracking susceptibility of materials.

[1] A solution with a boiling point of 154°C has a concentration of 45%. However, this expression has been adopted here in accordance with conventional usage.

* Numbers in the margin indicate pagination in the foreign text.

Therefore, in this report we investigated the effects of the component elements on stress corrosion cracking of austenitic stainless steels in boiling $MgCl_2$ solutions with various concentrations and studied the manner in which the effects of the component elements differed depending on the corrosion properties of the solution. At the same time, we considered the significance of using boiling 42% $MgCl_2$ solutions as a testing solution for accelerating stress corrosion cracking.

II. Materials Tested and Experimental Methods

1. Materials Tested

In order to examine the effects of the component elements, the following alloys were melted using a high-frequency induction furnace: those consisting basically of 18Cr-10Ni and varying the contents of C, Cu, N, P and minute amounts of Mo; those consisting basically of 17Cr-13Ni and varying the contents of Si and Mo; those consisting basically of 18Cr and varying the Ni contents; and those consisting basically of 10Ni and varying the Cr contents. Furthermore, since P remarkably increases the cracking susceptibility in a boiling 42% $MgCl_2$ solution [8], the P contents were adjusted so that it would be possible to observe the effects of the target components. The test pieces were first forged and hot rolled into plates 7 mm thick and then cold rolled to a thickness of 4.9 mm. Then they were given solution heat treatment at 1100°C x 30 min WQ, and tension type test pieces measuring 3 x 20 mm at their parallel parts were produced. For the SUS 304, 316, 321, and 347 stainless steels sold on the market and the Carpenter 20 steel, tension type test pieces as well as strip-shaped test pieces measuring 2 x 10 x 75 mm were similarly produced. After these test pieces had been polished with #0 emergy paper, they were given stress relief annealing at 1100°C x 10 min AC for the purpose of eliminating the effects of the machining. Furthermore, some of the strip-shaped test

pieces were given sensitization treatment at 650°C x 5 hours AC. /1321
Subsequently, in order to remove the surface films, the strip-shaped test pieces were polished lightly with #0 emery paper, and the tension type test pieces were electropolished in an aqueous solution of phosphoric acid, sulfuric acid, and chromic acid. Then they were tested. The chemical compositions of the test pieces are shown in Table 1, where are also given the tensile strength and proof strength measured using the tension type test pieces.

TABLE 1. CHEMICAL ANALYSES AND MECHANICAL PROPERTIES OF STEELS

Alloys	Chemical composition (wt%)										0.2% proof strength (kg/mm²)	Tensile strength (kg/mm²)
	C	Si	Mn	P	Cu	Ni	Cr	Mo	N	Othrs		
SUS 304(a)	0.053	0.52	1.69	0.023	0.03	9.39	19.13	0.05	0.031		—	—
SUS 304(b)	0.06	0.55	1.60	0.022	0.05	9.25	18.51	0.13	0.030		20.6	59.4
SUS 316(a)	0.052	0.33	1.65	0.020	0.22	13.49	16.46	2.11	0.022		—	—
SUS 316(b)	0.049	0.55	1.72	0.022	0.26	13.43	16.99	2.28	0.028		20.2	52.9
SUS 321	0.06	0.66	1.58	0.021	0.01	10.81	17.71	0.16	0.011	Ti 0.43	—	—
SUS 347	0.05	0.50	1.58	0.018	0.06	11.90	17.62	0.08	0.024	Cb 0.80	—	—
Carpenter 20	0.048	0.73	1.35	0.023	3.28	28.34	19.51	2.45	0.032	Cb 0.81	—	—
C-1	**0.032**	0.43	1.45	0.014	<0.01	10.00	17.93	<0.001	0.017		22.3	60.7
C-2	**0.11**	0.39	1.47	0.014	<0.01	10.25	17.70	<0.001	0.014		24.3	63.5
Si-1	0.05	**0.49**	1.55	0.018	<0.01	13.00	16.85	0.01	0.011		20.2	52.8
Si-2	0.054	**2.28**	1.51	0.015	<0.01	12.57	17.77	0.01	0.012		23.0	58.9
Cu-1	0.06	0.39	1.47	0.014	**<0.01**	10.25	17.83	<0.001	0.014		22.6	60.6
Cu-2	0.08	0.46	1.41	0.012	**1.07**	10.80	18.00	<0.001	0.016		19.5	51.8
Ni-1	0.07	0.50	1.42	0.016	<0.01	**13.33**	18.37	0.006	0.052		21.2	53.7
Ni-2	0.08	0.53	1.52	0.013	<0.01	**18.63**	18.40	0.004	0.018		20.2	53.2
Cr-1	0.06	0.46	1.37	0.010	<0.01	10.50	**15.62**	<0.001	0.015		24.0	60.8
Cr-2	0.06	0.46	1.38	0.012	<0.01	10.50	**19.85**	<0.001	0.015		25.0	59.7
Mo-1	0.048	0.51	1.42	0.006	<0.01	13.14	17.07	**<0.01**	0.022		16.3	53.4
Mo-2	0.050	0.46	1.44	0.006	<0.01	12.74	17.36	**0.96**	0.012		15.9	52.7
Mo-3	0.043	0.46	1.39	0.006	<0.01	13.23	16.78	**1.96**	0.020		17.7	52.8
N-1	0.07	0.52	1.54	0.007	<0.01	10.04	17.82	0.005	**0.029**		21.2	56.2
N-2	0.07	0.40	1.27	0.005	<0.01	10.30	17.84	0.004	**0.299**		38.8	71.7
A	0.06	0.46	1.49	**0.006**	<0.01	10.30	18.00	**<0.001**	0.014		18.6	55.3
B	0.07	0.61	1.55	**0.023**	<0.01	10.31	18.28	**0.005**	0.007		17.6	55.3
C	0.07	0.43	1.29	**0.002**	<0.01	10.49	17.73	**0.10**	0.031		20.3	58.3

2. Experimental Methods

The stainless steels available on the market were made into strip-shaped test pieces and given pretreatments as outlined above. These test pieces were bent in a U shape and constrained for 5 mm. Then they were immersed in a 20-45% boiling $MgCl_2$ solution and tested. They were checked for cracking at suitable time intervals. The concentration of the solution was adjusted by means of the boiling point. The testing time was 300 hours.

The effects of the component elements were studied by means of the tension type test pieces. Their cracking time was measured in boiling $MgCl_2$ solutions of various concentrations. The stress applied was mostly 25 kg/mm^2. For the 304 and 316 steels, we also measured the temporal changes in the natural potential after the stress had been applied. Saturated calomel electrodes were used as the reference electrodes. In cases when a saturated $MgCl_2$ solution at room temperature was used and when the test liquid had a concentration of less than 35%, the measurements were made through a $MgCl_2$ solution at room temperature having the same concentration as the test liquid.

III. Experimental Results

1. Stress Corrosion Cracking Susceptibility of Stainless Steels on the Market

(1) Effects of Concentration of Boiling $MgCl_2$ Solution

The U-bend method was used to study the effects of the concentration of the boiling $MgCl_2$ solution on the stress corrosion cracking of stainless steels sold on the market which had been given solution heat treatment or sensitization treatments. The results are as shown in Table 2. When the 304, 321, and 347 steels were given solution heat treatment, the lower limits of th/1322 the $MgCl_2$ concentration at which cracking occurred were 20-25%. On the other hand, the lower limit of concentration for the 316 steels, which have a high corrosion resistance, was 35%. In the case of the Carpenter 20 steel, cracking occurred only in a 45% $MgCl_2$ solution. There were almost no changes in the lower concentration limits for cracking when the steels were given

TABLE 2. EFFECT OF CONCENTRATION OF BOILING $MgCl_2$ SOLUTIONS ON STRESS CORROSION CRACKING OF COMMERCIAL ALLOYS BY U-BEND METHOD

Heat treatment	Alloys	Cracking time (hr) and fracture mode					
		45% $MgCl_2$	40% $MgCl_2$	35% $MgCl_2$	30% $MgCl_2$	25% $MgCl_2$	20% $MgCl_2$
Solution treatment	304 (a)	<5, T	<20, T	<20, T	<20, T	<100, T	<300*, T
	316 (a)	<30, T	<50, T	<200, T	N.C.	N.C.	N.C.
	321	<5, T	<20, T	<20, T	<20, T	<100, T	<300*, T
	347	<5, T	<20, T	<20, T	<20, T	<100, T	N.C.
	Carpenter 20	<80, T	N.C.	N.C.	N.C.	N.C.	N.C.
Sensitization	304 (a)	<5, T	<20, T	<20, T	<20, T	<100, TI	<100, TI
	316 (a)	<30, T	<50, T	<200, TI	N.C.	N.C.	N.C.
	Carpenter 20	<80, T	N.C.	N.C.	N.C.	N.C.	N.C.

(1) * : partly cracked
(2) T : Transgranular, I : Intergranular, TI : mixed crack, N.C. : not cracked in 300 hr test

sensitization treatment, but grain boundary cracking was observed as the concentration of the $MgCl_2$ solutions declined. In the 304 steels, grain boundary cracking was included at concentrations of 25% or less, and in the 316 steels, this was true with 35% $MgCl_2$. Cracking of 304 steel which had been given sensitizing treatment is shown in Photo 1.

The curves for the boiling point (concentration of boiling $MgCl_2$ solutions and the fracture time in 304 and 316 steels given solution heat treatment are shown in Figs. 1 and 2 for stresses of 25 kg/mm^2 and 15 kg/mm^2. At stress of 25 kg/mm^2, the minimum fracture time was displayed by the 304 steel at 140-150°C and by the 316 steel at about 150°C. These results differ from the linear relationships sought by Edeleanu [2]. When the 304 and the 316 steels are compared, no pronounced differences in the fracture times can be observed at high temperatures, but at temperatures of less than about 130°C, the stress corrosion cracking susceptibility of the 316 steel becomes remarkably greater than that of the 304 steel. When the stress applied is 15 kg/mm^2, the situation is different from that when the stress is 25 kg/mm^2. That is, at temperatures of more than about 150°C, the fracture

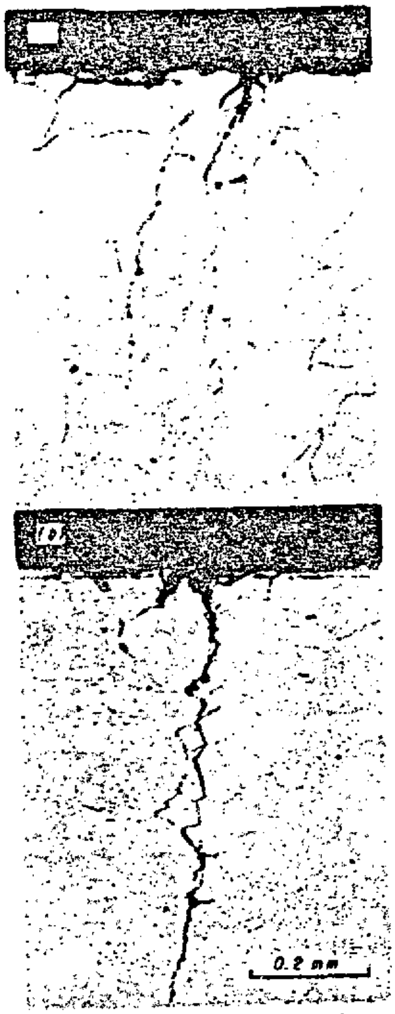

Photo.1 Stress corrosion cracking of sensitized 304 (a) stainless steel in boiling $MgCl_2$ solutions (a) 45% $MgCl_2$, (b) 20% $MgCl_2$

times of the 304 steel and the 316 steel are reversed, and 304 steel has a longer fracture time.

(2) Induction Time and Propagation Time of Stress Corrosion Cracking

When the curves for the boiling point (concentration) of the boiling $MgCl_2$ solutions and the fracture time of the 304 and 316 steels were sought, it was clearly established that the minimum value of the fracture time is displayed at a definite boiling point. One may /1323 suppose that convex curves are plotted at the bottom in this way because two contradictory factors were added together. Rooyen et al. [9, 10] measured the temporal changes of the natural potential while simultaneously performing micro-observations. As a result, no cracking could be observed before the peak potential was reached. Therefore, they divided the fracture time into two periods, calling the period before the peak potential the "induction time" and the period after it until fracture the "propagation time." The writers also measured the natural potential and sought the induction time (t_i) and the propagation time (t_p) for the 304 and 316 steels from the peak potential. The typical temporal changes of the natural potential in 304 steel after a stress of 25 kg/mm^2 was applied are shown in Fig. 3. As the boiling point (concentration) increases, the peak potential rises, and a longer time is required to reach the peak potential. The induction time, the propagation time, and the fracture time for 304 and 316 steels sought from the temporal

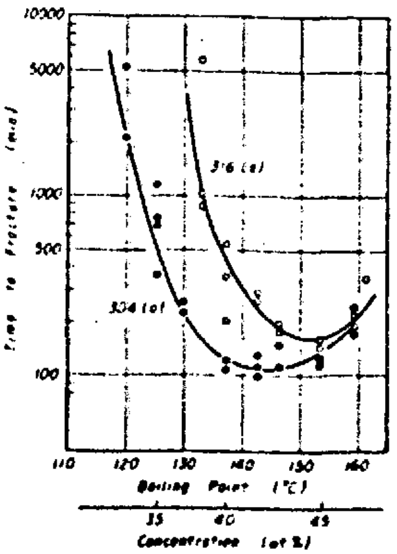

Fig.1 Fracture time of 304(a) and 316(a) stainless steels under the stress of 25 kg/mm² in various boiling point of $MgCl_2$ solutions

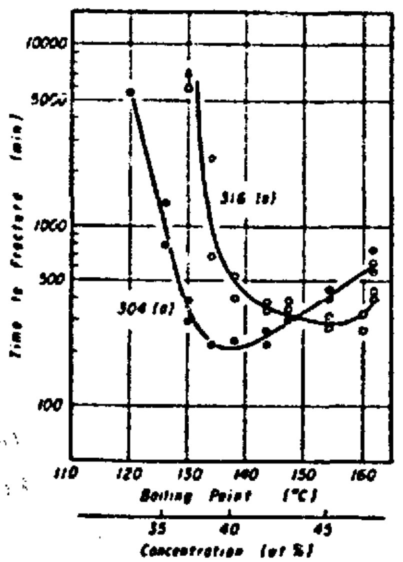

Fig.2 Fracture time of 304(a) and 316(a) stainless steels under the stress of 15 kg/mm² in various boiling point of $MgCl_2$ solutions

changes of the natural potential are shown in Figs. 4 and 5. In both 304 and 316 steels, a longer induction time is required as the boiling point (concentration) rises. On the other hand, the propagation time declines as the boiling point (concentration) increases; at 160°C, it is 30-40 min in 304 steel or 100-150 min in 316 steel. The fracture time is a combination of both these times. In the final results, 304 steel displays its minimum fracture time at 140-150°C, and 316 steel does so at about 150°C.

2. Effects of the Component Elements

The effects of the component elements on the stress corrosion cracking in boiling $MgCl_2$ solutions of various concentrations were studied in materials given solution heat treatment when a stress of 25 kg/mm^2 was applied.

(1) Effects of C

In a boiling 42% $MgCl_2$ solution, C causes a reduction of the cracking susceptibility [4-7]. In this report, the base alloy used was 18Cr-10Ni steel with the P content adjusted at 0.014% -- it being known that the P content exerts a remarkably adverse

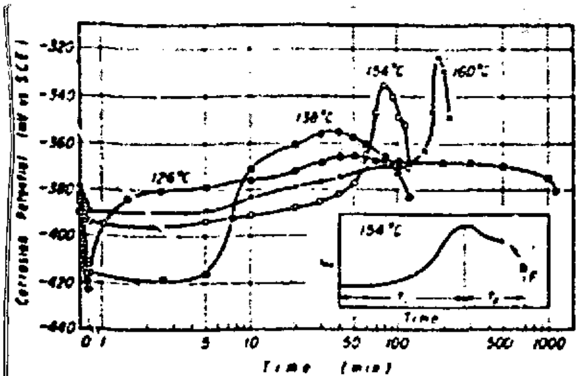

Fig.3 Effect of boiling point on corrosion potential-time curves of 304(b) stainless steel in boiling $MgCl_2$ solutions at 25 kg/mm²

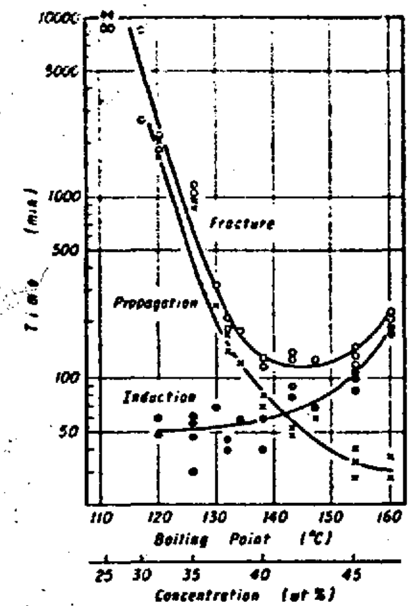

Fig.4 Induction, propagation and fracture time of 304(b) stainless steel in various boiling $MgCl_2$ solutions at 25 kg/mm²

influence on the cracking susceptibility [8]. Studies were made of two alloys with C contents of 0.032% and 0.11%. The results are shown in Fig. 6. Stainless steel with 0.032% C content displays the minimum fracture time at a temperature of about 140°C. On the other hand, when the C content is increased to 0.11%, the minimum fracture time is displayed at about 135°C, and the cracking susceptibility in boiling $MgCl_2$ solutions of higher than 140°C and lower than 125°C is remarkably reduced. However, no effect of C can be observed at temperature of 125-140°C.

(2) Effects of Si /1324

Si is an element which remarkably reduces the cracking susceptibility in a boiling 42% $MgCl_2$ solution [4-7], and various steels with a high Si content which are resistant to stress corrosion cracking have been developed. In this report, we studied two types of steel, consisting basically of 17Cr-13Ni steel with Si contents of 0.49% and 2.28%. The results are shown in Fig. 7. The stainless steel with a 0.49% Si content displays its minimum fracture time at about 140°C. On the other hand, when the Si content is 2.28%, the boiling point displaying the

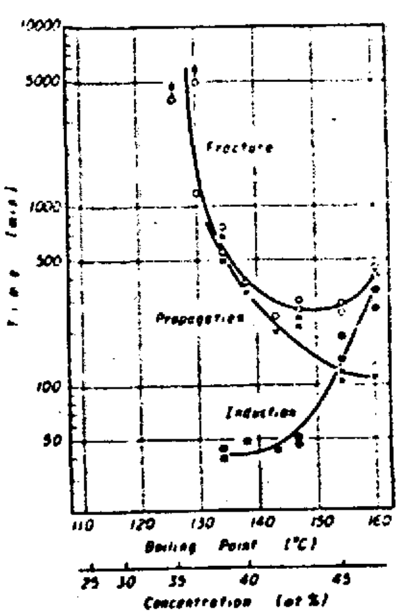

Fig.5 Induction, propagation and fracture time of 316(b) stainless steel in various boiling $MgCl_2$ solutions at 25 kg/mm²

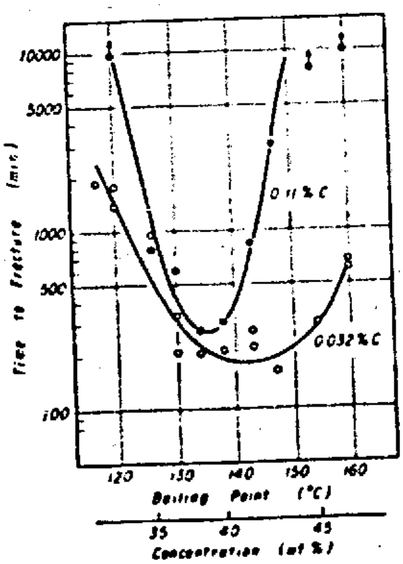

Fig.6 Effect of carbon content of 18Cr-10Ni stainless steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

minimum fracture time is lower (approximately 130°C), and the cracking susceptibility becomes remarkably small in boiling $MgCl_2$ solutions of 143°C or higher. However, no pronounced effects of Si can be observed at temperatures of less than 130°C.

(3) Effects of Cu

The effects of Cu were studied in two types of steels, consisting basically of 18Cr-10Ni steel with Cu contents of <0.01% and 1.07%. The results are shown in Fig. 8. In both steels, there is the minimum fracture time at about 150°C, and no pronounced effects of Cu can be observed at temperatures above 125°C. It is believed that this is because the adverse effects of Cu did not appear in the difference in cracking susceptibility since there was a somewhat high content of P, which functions to increase greatly the cracking susceptibility in $MgCl_2$ solutions of a high concentration [8]. On the other hand, at temperatures lower than 125°C, Cu is observed to have a tendency to reduce the cracking susceptibility.

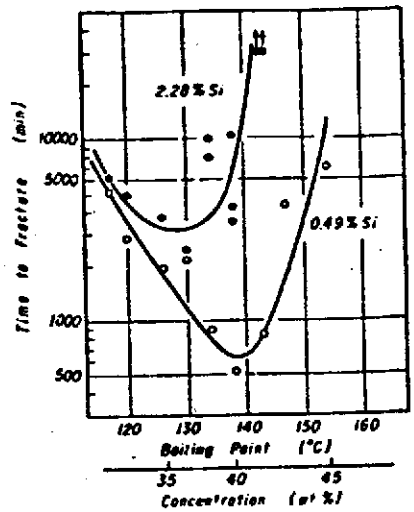

Fig.7 Effect of silicon content of 17Cr-13Ni stainless steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

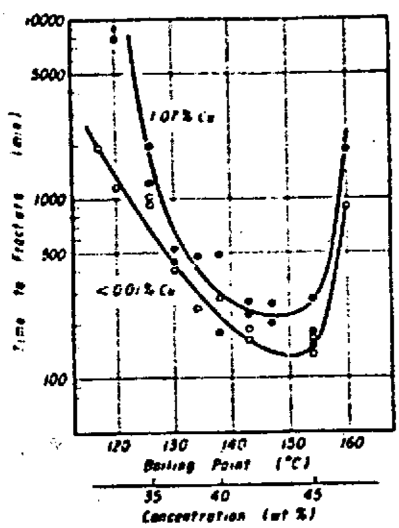

Fig.8 Effect of copper content of 18Cr-10Ni stainless steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

(4) Effects of Ni

In order to elucidate the effects of Ni on stress corrosion cracking, we studied three types of steel consisting basically of 18% Cr with Ni contents of 10.25%, 13.33% and 18.63%. The results are shown in Fig. 9. The stainless steel with 10.25% Ni and that with 13.33% Ni display their minimum fracture time at 140-150°C. Increases in the Ni content cause reductions of the cracking susceptibility, but this effect is most pronounced at 145-155°C, while the effect of Ni is no longer pronounced at temperature of less than 130°C. When the Ni content increases further to 18.63%, the cracking susceptibility will decrease remarkably.

(5) Effects of Cr

In order to elucidate the effects of the Cr content on stress corrosion cracking, we studied two types of steel consisting basically of 10% Ni, with Cr content of 15.62% and 19.85%. They were studied in boiling $MgCl_2$ solutions of various concentration. The results are shown in Fig. 10. The stainless steel with 19.85% Cr displays its minimum fracture time at about 150°C. On the other hand, when there is a 15.62% Cr

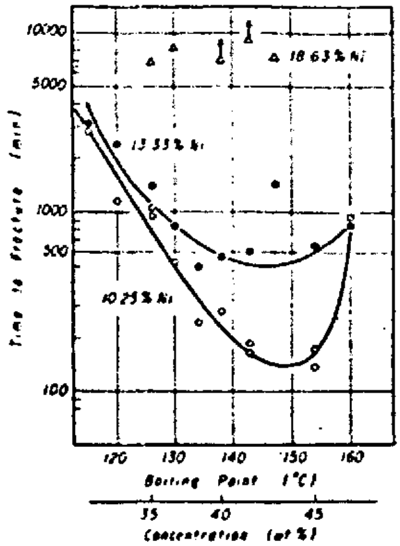

Fig.9 Effect of nickel content of Fe-18Cr base steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

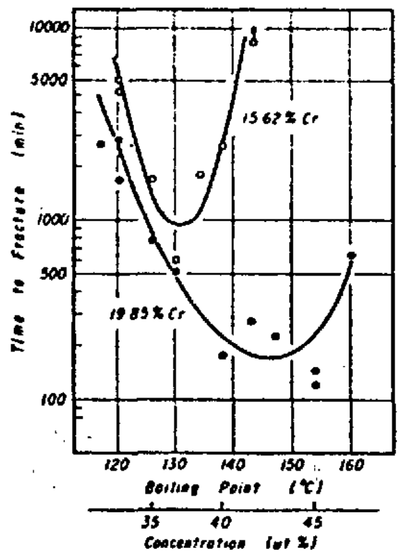

Fig.10 Effect of chromium content of Fe-10 Ni base steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

content, the minimum fracture time is /1325 displayed at about 130°C, and there is a remarkable reduction of the cracking susceptibility in boiling $MgCl_2$ solutions of 42% or higher. However, no pronounced effect of Cr can be observed at less than 130°C.

(6) Effects of Mo

In order to elucidate the effects of Mo, we studied three types of steel consisting basically of 17Cr-13Ni steel, with Mo contents of <0.01%, 0.96%, and 1.96%. The results are shown in Fig. 11. The stainless steel with <0.01% Mo breaks at about 140°C, while cracking does not occur at higher or lower temperatures than this, and a high resistance to stress corrosion cracking susceptibility is displayed. However, this is so because there is a low P content (0.006%), which is known to remarkably increase the cracking susceptibility, in comparison with the stainless steels sold on the market [8]. When the Mo contents are 0.96% or 1.96%, the cracking susceptibility at high temperatures will increase rapidly, and the boiling points displaying the minimum fracture time will be 150-160°C. However, when the 0.96% Mo steel and the 1.96% Mo steel are compared at temperatures

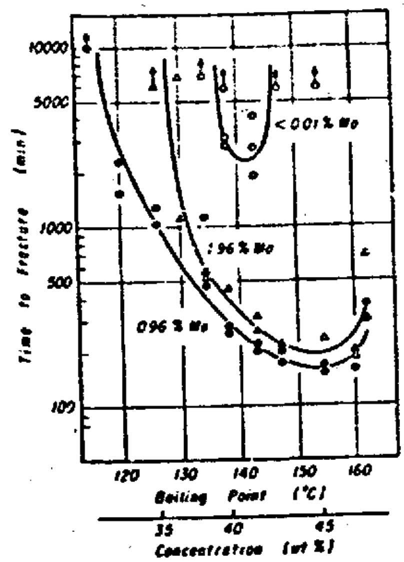

Fig.11 Effect of molybdenum content of 17Cr-13Ni stainless steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

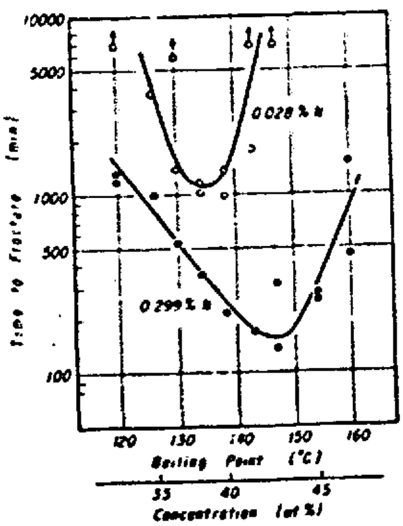

Fig.12 Effect of nitrogen content of 18Cr-10Ni stainless steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

of less than 130°C, the stainless steel with the higher Mo content has a remarkably improved resistance to stress corrosion cracking susceptibility.

(7) Effects of N

The effects of N were studied for two types of steel consisting basically of 18Cr-10Ni steel, with N contents of 0.028% and 0.299%. They were studied in boiling $MgCl_2$ solutions of various concentrations. The results are shown in Fig. 12. Since the stainless steel with a 0.028% N content has a low content of impurities such as P or Mo, cracking does not occur at higher than 147°C, but fracture occurs at 130-140°C. On the other hand, in the stainless steel with a 0.299% N content, the boiling point displaying the minimum fracture time shifts towards the higher temperatures (about 150°C), and fracture occurs within a short time in a boiling 42% $MgCl_2$ solution.

(8) Effects of P and Minute Quantities of Mo

The stainless steels sold on the market ordinarily contain about 0.02% P and 0.05-0.3% Mo as impurities. It has also been clearly established that these impurities such as P and minute

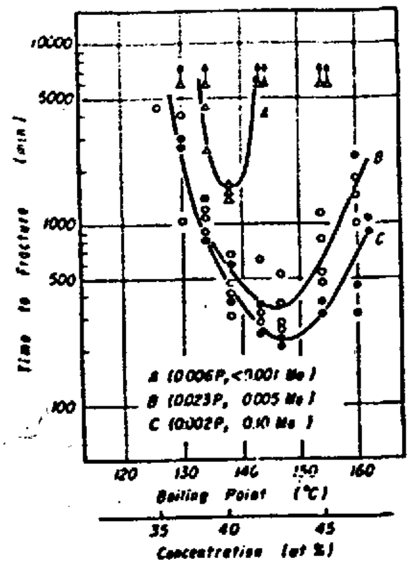

Fig. 13 Effects of phosphorus and molybdenum contents of 18 Cr-10 Ni stainless steels on the boiling point-time to fracture curves in $MgCl_2$ solutions at 25 kg/mm²

quantities of Mo remarkably increase the cracking susceptibility in boiling 42% $MgCl_2$ solutions [7, 8]. In this report we studied the effects of P and minute quantities of Mo in three types of steel consisting basically of 18Cr-10Ni steel with the following impurities: (0.006% P, <0.001% Mo), (0.023% P, 0.005% Mo), and (0.002% P, 0.10% Mo). The results are shown in Fig. 13. /1326
The steels with reduced P and Mo contents will undergo fracturing at 138°C (40% $MgCl_2$) but will become rapidly immune to cracking at temperatures higher or lower than this. They are immune in the boiling 42% $MgCl_2$ solutions which are commonly used as testing solutions accelerating stress corrosion cracking. On the other hand, in stainless steel containing 0.023% P or 0.10% Mo, the boiling point displaying the minimum fracture shifts towards the higher temperatures (140-150°C), and the cracking susceptibility will become remarkably high in boiling 42% $MgCl_2$ solutions. The adverse effects of P and minute quantities of Mo are especially pronounced at temperatures higher than 140°C.

IV. Discussion

When the effects of the concentration of the boiling $MgCl_2$ solution on stress corrosion cracking of the stainless steels available on the market were studied, it was observed as a result that, as the concentration of the boiling $MgCl_2$ solutions decreases, grain boundary cracking occurs in the 304 and 316 steels given sensitizing treatment. Grain boundary cracking occurred in 304 steels at concentrations of 25% or less, while it occurred in

316 steels at a higher concentration than in the 304 steels (35%). Okada et al. [11] studied the various factors affecting the forms of the cracks and reported that grain boundary cracking tends to occurs more readily when the Mo content is increased or when negative polarization occurs while at the same time the concentration of the boiling $MgCl_2$ solution is lowered. It is believed that the fact that grain boundary cracking tends to occur more easily as the concentration of the boiling $MgCl_2$ solution is lowered may be explained by the fact that the corrosiveness of the solution is weakened, producing conditions which cause elution to occur preferentially at the grain boundary part, as compared with the interior of the grain. The fact that grain boundary cracking occurs in 316 steel in boiling $MgCl_2$ solutions with a higher concentration than is the case in 304 steels, as Okada et al. have also pointed out, is because the corrosion resistance is relatively increased because Mo is contained. It has been reported [12] that when sensitization is performed, grain boundary cracking tends to occur more easily in boiling 20% NaCl solutions. These results can also be explained from the fact that grain boundary cracking tends to occur more readily when the corrosiveness of the solution weakens.

Many attempts have been made to separate the induction time (t_i) and the propagation time (t_p) of stress corrosion cracking, for instance by measuring the potential-time curves or by measuring the changes in elongation [9, 10, 13-15]. However, opinions differ among researchers concerning the point in time at which the propagation period may be regarded as beginning. The writers measured the temporal changes of the natural potential. They separated t_i and t_p at the point of time when destruction of the film took precedence over its repair and when the potential began to drop continuously, that is, at the peak potential. The results for 304 steel and 316 steel are shown in Figs. 4 and 5. That is, the results for the 304 steel were 120-160°C, and the results for the 316 steel were 134-160°C. At temperatures lower than these, there were few changes in the potential, and separation was impossible. However, since not even microscopic cracks can be observed after testing of 304 steel at 111°C or of 316 steel at 126°C, it is thought that the minimum value of the induction time for 304 steel is present at about 120°C, and that for 316 steel is present at about 130°C. The induction time for cracking with reference to the boiling point of the boiling $MgCl_2$ solution is represented schematically in Fig. 14. The minimum value of the induction time is displayed in a solution having a definite corrosiveness, while the boiling point (concentration) displaying the minimum value differs depending upon the corrosion resistance properties of the materials. This indicates that stress corrosion cracking depends on the relative connections between the repair velocity and the destruction velocity of the film [6]. It is believed here that cracking cannot occur in zone (I) because the corrosiveness of the solution is /1327 too weak and the repair velocity of the film is too rapid, and that it cannot occur in zone (III) because there is a strong corrosiveness, and there are overall corrosive properties. It is believed that, in order for cracking to occur in zone (I), it is necessary either for the pH to decline or for oxidizing agents such as dissolved oxygen to be present. On the other hand, as has already been mentioned, the fracture time displays its minimum value because the fracture time is expressed as the total of the induction time and the propagation time of cracking. The boiling point (concentration) displaying the minimum fracture time shifts depending upon the elements added because the component elements

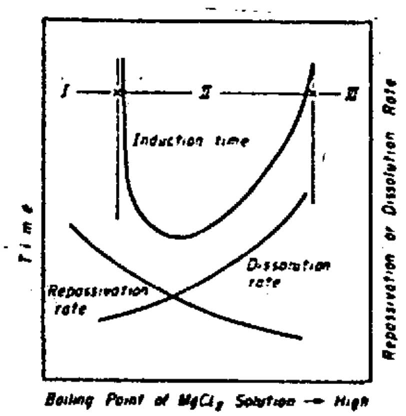

Fig.14 Schematic figure illustrating corrosion condition for stress corrosion cracking

influence each other with respect to the induction time and the propagation time, respectively.

There are many reports concerning the effects of the component elements on stress corrosion cracking, but they deal mostly with results obtained in boiling 42% $MgCl_2$ solutions. In this report, we studied the effects of the component elements on stress corrosion cracking mainly in austenitic stainless steels consisting basically of 17Cr - (10-13)Ni steel. The studies were made in boiling $MgCl_2$ solutions of various concentrations. Next, on the basis of these results, let us make comparative studies of the manner in which the effects of the component elements vary depending upon the concentration of the $MgCl_2$ solution, taking the effects of the component elements in boiling 42% $MgCl_2$ solutions as the standard.

On the basis of results obtained in boiling 42% $MgCl_2$ solutions, C is regarded as being an element which brings about a remarkable reduction of the stress corrosion cracking susceptibility [4-7, 16, 17], although there are also reports indicating that there is the greatest cracking susceptibility when the C contents are 0.06-0.1% [18-20]. It is believed that this is so because C operates as an austenite stabilizing element while it also converts the dislocation distribution into a cellular distribution [21, 22]. In the results obtained in these experiments as well, C caused remarkable reductions of the cracking susceptibility in boiling $MgCl_2$ solutions of more than 140°C; these results coincided with the past results obtained in boiling 42% $MgCl_2$ solutions. However, no effects of C can be observed at temperatures of 125-140°C. From the phenomenal standpoint, the effects of C act to expand zone (III) in Fig. 14 in the direction of the lower temperatures. On the other hand, C also causes pronounced reductions in the cracking susceptibility at temperatures of lower than 125°C. However, as was already mentioned, when the concentration of the boiling $MgCl_2$ solution decreases, grain boundary cracking tends to occur easily; therefore, the effects of C on the cracking susceptibility will differ under conditions where sensitization takes place and Cr-starved parts are formed. That is, the greater is the C content, the greater will be the extent of the Cr-starved parts which are formed, and the greater will be the susceptibility to grain boundary cracking. Since C is an element which is effective with respect to cracking inside the grain but which, on the contrary, is harmful with respect to grain boundary cracking, the cracking susceptibility is determined by means of the combination of both [23].

Si is another element which causes pronounced reduction of the cracking susceptibility in boiling 42% $MgCl_2$ solutions (4-7, 19, 20, 24]. When Si is added at concentrations of 1.5-2.0% or higher, almost no stress corrosion cracking will occur. In the results of these experiments as well, Si brought about pronounced reductions in the cracking susceptibility in boiling 42% $MgCl_2$ solutions. However, no pronounced effects of Si can be observed at temperatures of less than 130°C. It is believed that the fact that the cracking susceptibility is reduced remarkably in boiling 42% $MgCl_2$ solutions does not have anything to do with structural considerations [21]. Rather, it is believed that Si accelerates active resolution, and the protective properties of the film decline [7].

Concerning Cu, there are reports which hold that in boiling 42% $MgCl_2$ solutions it somewhat increases the cracking susceptibility [7], but in other reports it is argued that it has almost no effects on the cracking susceptibility [18, 25]. In the results of these experiments as well, in boiling 42% $MgCl_2$ solutions, no difference could be observed in the cracking susceptibility between <0.01% Cu and 1.07% Cu. However, this is so because there is a somewhat high content of P, which causes a pronounced increase in the cracking susceptibility. It is believed that the adverse effects of Cu appear when the P contents are lowered [7]. On the other hand, at temperatures lower than 125°C, Cu was observed to have the effect of reducing the cracking susceptibility. These results coincide with the results showing that Cu causes a pronounced reduction of the cracking susceptibility, in boiling 20% NaCl solutions, which are only weakly corrosive [23]. This is believed to be on account of Cu's effect in improving the corrosion resistance properties [7].

There are many reports concerning the effects of Ni. All the reports agree that, when the Ni contents are increased, the alloys become immune to cracking [1-3, 5, 19, 20, 24]. However, the amounts of Ni which give immunity differ depending upon differences in the basic components or the amounts of impurities such as P or N. Among the possible causes of the effects of Ni are the effects on both the structural [21, 26, 27] and the electrochemical [6, 28] aspects. In the effects of these experiments as well, Ni brought about reductions in the cracking sus- /1328
ceptibility. However, it became clear that this effect is most pronounced at temperatures of 145-155°C and that the effect ceases to be pronounced at low temperatures. Ni differs from the other component elements in that it displayed no tendency to cause shifts of the boiling point (concentration) displaying the minimum fracture time.

The effects of Cr differ depending upon the amounts of Ni present. In the results obtained in boiling 42% $MgCl_2$ solutions, some reports indicate that it somewhat increases the cracking susceptibility [24], while there are other reports indicating that the maximum cracking susceptibility occurs at a Cr concentration of about 20% [25]. It was learned as a result of these experiments that in boiling 42% $MgCl_2$ solutions increases of the Cr content led to increases in the cracking susceptibility, but that no pronounced effects of the Cr could be observed at temperatures of less than 130°C. The effects when the Cr contents were reduced tended to be the same as the effects when the Si contents were increased, as described above. It is believed that the decline of the cracking susceptibility in boiling 42% $MgCl_2$ solutions when the Cr content is reduced is because the corrosion resistance declines and the protective properties of the film decrease [7].

It has been reported that Mo is a harmful element for stress corrosion cracking in boiling 42% $MgCl_2$ solutions and that the cracking susceptibility will increase remarkably when even 0.1-0.2% of it is contained as an impurity [5, 7, 16]. However, there are also reports stating that there is the greatest cracking susceptibility at Mo contents of 1-2%, but that, on the contrary, cracking susceptibility declines at contents greater that this [18]. On the other hand, it is reported that, in 20% NaCl solutions, Mo is an element which causes remarkable reductions in the cracking susceptibility [29]. The effects of Mo differ depending upon the environment. In these experiments, we studied the effects of Mo in 17Cr-13Ni steels and the effects of minute quantities of Mo in 18Cr-10Ni steels. It was ascertained, as a result, that in boiling 42% $MgCl_2$ solutions Mo causes pronounced increases in the cracking susceptibility. On the other hand, when the effects of Mo at temperatures lower than 130°C are examined, it is clear that stainless steels containing no Mo at all display the smallest susceptibility to cracking. However, when 0.96% Mo and 1.96% Mo stainless steels are compared, it is obvious that Mo causes a reduction of the cracking susceptibility. This coincides with the differences in the susceptibility to stress corrosion cracking between 304 steels and 316 steels at temperatures lower than 130°C, as mentioned above. This indicates that there is an Mo quantity in the vicinity of 1% at which the cracking susceptibility is increased to the maximum in a 130°C solution. The fact that the cracking susceptibility is increased by Mo concentrations of up to 1% is probably explained by the fact that Mo acts to change the dislocation arrangement into a planar one [28, 30]. On the other hand, it is believed that the fact that the cracking susceptibility is reduced by Mo concentrations of more than 1% may be explained by the fact that the improvement of the corrosion resistance brought about by Mo has a pronounced effect on the cracking susceptibility [7]. Naturally, the amounts of Mo which increase the cracking susceptibility to the greatest degree differ depending upon the corrosive properties of the solution.

It has been observed that N is harmful [5, 16, 17, 19, 20]. The possible explanations for this may be that it acts to convert the dislocations into planar ones [21, 28] or that it increases the cracking susceptibility by segregating in the dislocations [31, 32]. It was also confirmed in the results of these experiments that N increases the cracking susceptibility. However, the adverse effects of N are less than those of P.

P is an element which remarkably increases the cracking susceptibility. The writers [8] examined the effects of P and N in 18Cr-10Ni steels in boiling $MgCl_2$ solutions of 154°C. They stated that when the P content is less than 0.003%, there will be immunity to stress corrosion cracking regardless of the N contents. They reported that the fact that P causes an increase in the cracking susceptibility is attributable to the fact that it converts the dislocation arrangement into a planar one, while at the same time heightening the protective properties of the film and accelerating local corrosion. It has also been observed that when the P contents increase there occurs elution with a specific crystalline orientation [33]. In the course of these experiments as well, it was ascertained that, when the P contents are reduced, this will reduce the cracking susceptibility, especially in boiling $MgCl_2$ solutions with concentrations of 42% or greater.

However, cracking will begin to occur when the concentration is lowered, such as in boiling 40% $MgCl_2$ solutions (138°C), and the corrosive properties are somewhat weakened. This shows that the relative velocity of film repair and elution in these solutions provides corrosion conditions favorable for the occurrence of cracking.

On the basis of the boiling point (concentration) / fracture time curves of the boiling $MgCl_2$ solutions for the component elements studied in the preceding (C, Si, Cu, Ni, Cr, Mo, N, and P), it is possible, on the phenomenal level, to classify these elements into the following three types. One type consists of C and Si. The greater is the amount of these elements contained, the farther the boiling point displaying the minimum fracture time moves towards the lower temperatures, and the less will be the cracking susceptibility in boiling 42% $MgCl_2$ solutions. This fact means that C and Si expand zone III in Fig. 14, spreading it out towards the lower temperature region. However, Si does not exert a great influence on the cracking susceptibility at a point below the boiling point (concentration) displaying the minimum fracture time. A second type includes Cu, Cr, Mo, N, and P. As the contents of these elements increase, the farther will the boiling point displaying the minimum fracture time move towards the higher temperatures, causing a pronounced increase in the cracking susceptibility in boiling 42% $MgCl_2$ solutions. However, although Mo and Cu improve the corrosion resistance, at lower temperatures they act to reduce the crack susceptibility. This means that they expand zone I in Fig. 14, spreading it out towards the higher temperatures. A third type is Ni. This element causes a reduction of the cracking susceptibility throughout the entire temperature range without causing any shifts of the boiling point (concentration) displaying the minimum fracture time. However, its effect is most pronounced at 145-155°C.

V. Conclusion

In order to elucidate the effects of the component elements on the stress corrosion cracking of austenitic stainless steels, we studied the properties of stainless steels sold on the market and the effects of component elements such as C, Si, Cu, Ni, Cr, Mo, N, P, and minute quantities of Mo in boiling $MgCl_2$ solutions of various concentrations. The following facts were clearly established as a result.

(1) Studies of the stress corrosion cracking susceptibility of stainless steels sold on the market revealed the following:

(i) The lower limits of the $MgCl_2$ concentration at which cracking occurred in 304, 321, and 347 steels were 20-25%. On the other hand, the lower limit was 35% $MgCl_2$ in 316 steels, which /1329 have a higher corrosion resistance. In Carpenter 20 steel, cracking would occur only in a 45% $MgCl_2$ solution.

(ii) As the concentration of the boling $MgCl_2$ solutions decreased and the corrosive properties weakened, grain boundary cracking occurred in sensitized 304 and 316 steels. Grain boundary cracking occurred in 316 steels, which have a high corrosion resistance, in $MgCl_2$ solutions having higher concentrations than in the case of 304 steels.

(2) The induction time and propagation time of cracking were separated on the basis of the temporal changes in the natural potential of the 304 and 316 steels and on the basis of microscopic observations. The relationships with the boiling points of the boiling $MgCl_2$ solutions were then sought. The following findings were obtained as a result.

(i) It is believed that the minimum value of the induction time is displayed at about 120°C in 304 steels and at about 130°C in 316 steels. On the other hand, the propagation time becomes shorter as the boiling point rises.

(ii) The fact that the boiling point (concentration) / fracture time curves of boiling $MgCl_2$ solutions display a minimum value is because the fracture time is expressed as the sum of these.

(3) The boiling point (concentration) / fracture time curves of the boiling $MgCl_2$ solutions were sought for various types of stainless steel in which the contents of the component elements were varied. As a result, it was clearly established that they can be classified into the following three types of elements.

(i) C and Si cause the boiling point displaying the minimum fracture time to shift towards the lower temperatures and cause the cracking susceptibility in boiling 42% $MgCl_2$ solutions to decline. However, at lower temperatures, Si does not have a great influence on the cracking susceptibility.

(ii) Mo, N, P, Cr and Cu cause the boiling point displaying the minimum fracture time to shift towards the higher temperatures and cause an increase of the cracking susceptibility in boiling 42% $MgCl_2$ solutions. However, Mo and Cu cause a decrease of the cracking susceptibility at low temperatures.

(iii) Ni causes a decrease of the cracking susceptibility throughout the entire temperature region without causing any shifts of the boiling point displaying the minimum fracture time.

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